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Gallium Hydrides with a Radical-Anionic Ligand

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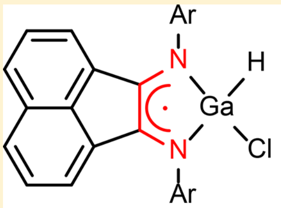
Supporting Information



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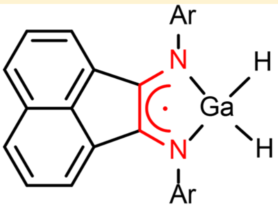

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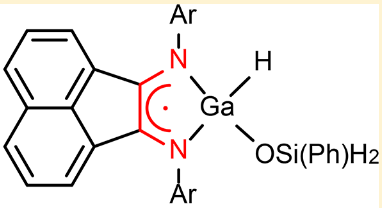

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ABSTRACT: The reaction of Cl_2GaH with a sodium salt of the dpp-Bian radical-anion (dpp-Bian$^{\bullet-}$)Na (dpp-Bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) affords paramagnetic gallane (dpp-Bian$^{\bullet-}$)Ga(Cl)H (**1**). Oxidation of (dpp-Bian^{2-})Ga−Ga(dpp-Bian^{2-}) (**2**) with N_2O results in the dimeric oxide (dpp-Bian$^{\bullet-}$)Ga(μ^2-O)$_2$Ga(dpp-Bian$^{\bullet-}$) (**3**). A treatment of the oxide **3** with phenylsilane affords paramagnetic gallium hydrides (dpp-Bian$^{\bullet-}$)GaH_2 (**4**) and (dpp-Bian$^{\bullet-}$)Ga{OSi(Ph)H_2}H (**5**) depending on the reagent's stoichiometry. The reaction of digallane **2** with benzaldehyde produces pinacolate (dpp-Bian$^{\bullet-}$)Ga($O_2C_2H_2Ph_2$) (**6**). In the presence of $PhSiH_3$, the reaction between digallane **2** and benzaldehyde (**2**: $PhSiH_3$: PhC(H)O = 1:4:4) affords compound **4**. The newly prepared complexes **1**, **3**−**6** consist of a spin-labeled diimine ligand−dpp-Bian radical-anion. The presence of the ligand-localized unpaired electron allows the use of the ESR spectroscopy for characterization of the gallium hydrides reported. The molecular structures of compounds **1**, **3**−**6** have been determined by the single-crystal X-ray analysis.

INTRODUCTION

The gallium hydrides are extensively explored within the Group 13 metals hydride chemistry.[1−4] These compounds attract a significant attention in terms of their practical application and fundamental aspects. For instance, volatile Lewis acid−base adducts of GaH_3 and some related hydridogallium derivatives are considered as potential easy-to-handle sources for preparation of GaN and GaAs films or nanoparticles in MOCVD processes.[2,5−8] Also, dichlorogallane Cl_2GaH,[9−11] dialkyl-,[12−14] and diarylgallanes[15−17] react with unsaturated substrates (ketones, nitriles, olefins, and alkynes) by addition of the Ga−H bond across the multiple bond to result in hydrogallation products.[4,10,12,18−26] Hydrometalation reactions of substituted alkynes by dichloro- or dialkylgallanes have been investigated in detail, and the diversity of the reactions pathways and the frameworks of the formed gallium-containing compounds were shown.[4,18−26] Sometimes, hydrogallation reactions proceed more selectively compared to hydroalumination processes.[3,4]

Monomeric gallium hydrides supported by the bidentate *N*,*N*-ligands represent an interesting class of metal hydrides.[27−35] One may expect a high reactivity of these species toward oxidants, unsaturated substrates as well as acids E−H (E = C, N, P, O, S). Stepwise hydrolysis of β-1,3-diketiminate derivative (dpp-nacnac)GaH_2 (dpp = 2,6-$i$$Pr_2C_6H_3$) affords initially (dpp-nacnac)Ga(OH)H, and then (dpp-nacnac)Ga(OH)$_2$.[32] Carbon dioxide inserts into Ga−H bond of (dpp-nacnac)Ga(tBu)H to result in a formic acid derivative (dpp-nacnac)Ga(tBu){OC(O)H}, which reacts with boron pinacolate (pin)BH (pin = $OCMe_2CMe_2O$) to afford boron formiate (pin)B{HC(O)O} and starting (dpp-nacnac)Ga(tBu)H.[34] Furthermore, the latter complex catalyzes addition of (pin)BH to CO_2,[34] thus demonstrating perspectives of application of the main-group metal derivatives as catalysts in chemical syntheses.

In the mentioned catalytic carboxylation reaction, the active site of (dpp-nacnac)Ga(tBu)H is represented by the metal−hydrogen bond, while no structural or redox transformation happens with the *N*,*N*-ligand. In contrast, a series of organic molecules that may serve well as redox-active ligand in complexes with metals have been reported. These molecular systems have been intensively studied in the last years with the aim to develop new catalytic systems.[36−41] Redox-active ligands allow a significant extension of reactivity of the metal complexes. For instance, because of reversible electron transfer from/to redox-active ligand, the oxidative addition/reductive elimination processes become possible even with redox-inactive main group metals. In some of these labile metal complexes, the ligands, besides the metal, participate directly in the formation

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of new chemical bonds. As for the transition-metal-based catalysts, a chemical cooperation between the metal and redox-active ligand can be influenced with the spectator group present in the metal coordination sphere.

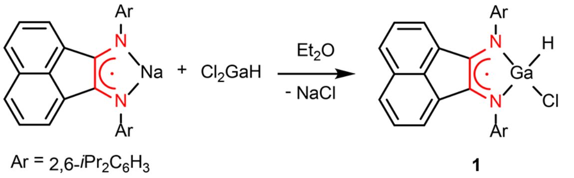
To date, gallium complexes of the redox-active iminopyridines,[42,43] diazadienes,[44−50] and 1,2-bis(imino)acenaphthenes[51−55] have been reported. Often they react through electron transfer from/to the redox-active ligand. In some cases, their reactions results in direct chemical bonds between the ligand and substrate.[42,43,48−50,53−65] For instance, gallium complexes of a dianion of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-Bian) react with alkynes[55,64,65] and enones[55] to afford cycloadducts. In the course of these reactions, new bonds between the substrates and metal as well as ligand are formed. Surprisingly, the newly formed bonds are labile enough to eliminate the unchanged substrate and the starting gallium compound with an increase in temperature.

One may suggest that gallium hydrides coordinated to redox-active dpp-Bian may disclose a rich chemistry due to the presence of two different reactive sites: gallium−hydrogen bond and redox-active dpp-Bian ligand. Depending on the reagents, one of two reactive sites in the redox-active gallium hydrides can be involved in the reaction. Since both of the reactive sites are sensitive toward unsaturated substrates, one can expect the respective chemoselectivity. On the other hand, the presence of the two reactive centers in the molecules may allow a series of the chemical successive processes on a single coordination compound. In this paper, we report on the synthesis of gallium hydrides supported with radical-anion of dpp-Bian, (dpp-Bian$^{\bullet-}$)Ga(X)H (**1**: X = Cl; **4**: X = H; **5**: X = OSi(Ph)H_2) as well as on the preparation and characterization of paramagnetic gallium oxide (dpp-Bian$^{\bullet-}$)Ga(μ^2-O)$_2$Ga(dpp-Bian$^{\bullet-}$) (**3**) and gallium pinacolate (dpp-Bian$^{\bullet-}$)Ga($O_2C_2H_2Ph_2$) (**6**) using (dpp-Bian^{2-})Ga−Ga(dpp-Bian^{2-}) (**2**) as starting reagent. Also, we report on the attempted synthesis of gallium hydride coordinated to dpp-Bian dianion.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Compounds 1, 3, 4, 5, and 6. The reaction of Cl_2GaH with (dpp-Bian$^{\bullet-}$)Na (in situ from dpp-Bian and one molar equivalent of Na metal in Et_2O) affords paramagnetic gallane (dpp-Bian$^{\bullet-}$)Ga(Cl)H (**1**). Compound **1** has been isolated from toluene as brown prismatic crystals in 73% yield (Scheme 1).

Scheme 1. Synthesis of Compound 1



In the IR spectrum, the Ga−H bond in complex **1** gives rise to the absorption at 1951, 1893, and 1866 cm^{-1}, which is well compared with that in the IR spectra of Cl_2GaH[9,11] and gallium hydrides coordinated to dianionic dad ligands.[27,29] Because of the presence of the dpp-Bian radical-anion, compound **1** exhibits a well-resolved isotropic ESR signal in toluene (Figure 1). Its hyperfine structure reflects coupling of an unpaired electron to one proton, to two equivalent ^{14}N nuclei, to ^{35}Cl and ^{37}Cl magnetic isotops as well as to magnetic isotops ^{69}Ga and ^{71}Ga.

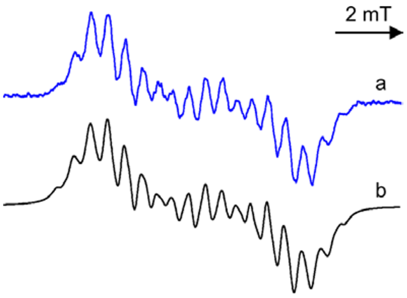
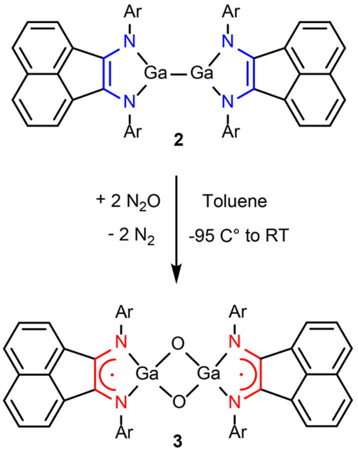


Figure 1. ESR spectrum of compound **1** (toluene, 298 K): (a) experimental; (b) simulated (a_i(2 × ^{14}N) = 0.476, a_i(^1H) = 0.590, a_i(^{35}Cl) = 0.219, a_i(^{37}Cl) = 0.183, a_i(^{69}Ga) = 1.423, a_i(^{71}Ga) = 1.807 mT; g = 2.0021).

Despite the presence of a Ga−H bond, compound **1** is unreactive toward styrene, hepten-1, vinyl-*n*-butyl ether, and phenylacetylene. With these substrates, compound **1** does not react even at reflux in toluene. An inertness of the dpp-Bian radical-anion in compound **1** toward unsaturated substrates (e.g., phenylacetylene) is expected because the cycloaddition of the alkynes to dpp-Bian gallium derivatives occurs only when the dpp-Bian acts as dianionic ligand. So, with dimethylacetylenedicarboxylate complex, **1** reacts through oxidation of the dpp-Bian radical-anion resulting in free dpp-Bian.

Looking for the synthetic approach to gallium dihydride supported by dpp-Bian ligand, we have reacted (dpp-Bian$^{\bullet-}$)-GaX_2 (X = Cl,[54] I[51]) with alkali metal hydrides MH (M = Na, K). Although these reactions proceed in coordinating solvents, the desired product could not be isolated. Bearing in mind that gallium is not as oxophilic compared to some other main group elements, we decided to synthesize gallium oxo-derivative and then react it with aluminum or silicon hydrides. As intended, oxidation of (dpp-Bian^{2-})Ga−Ga(dpp-Bian^{2-}) (**2**) with N_2O in toluene resulted in an oxo-bridged compound (dpp-Bian$^{\bullet-}$)-Ga(μ^2-O)$_2$Ga(dpp-Bian$^{\bullet-}$) (**3**) (Scheme 2). An increase in the temperature of the reaction mixture from −95 to 20 °C was accompanied by a color change from deep blue to red-brown. Evolution of gaseous nitrogen was also observed. Oxide **3** has been isolated in a form of deep green rhombohedra in 72% yield.

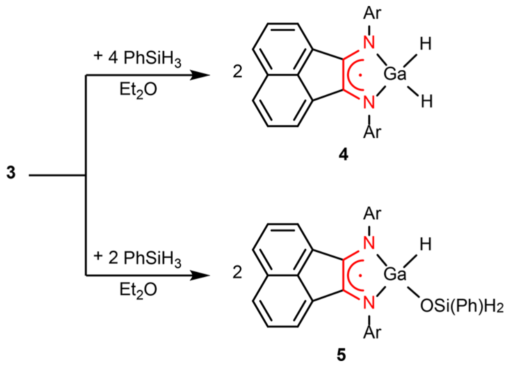
Scheme 2. Synthesis of Compound 3 via Oxidation of Digallane 2 by N_2O



For the formation of Ga−O bonds, digallane **2** recruits the electrons from the metal−metal bond as well as from dianionic dpp-Bian ligands that undergo oxidation to radical-anions in the course of the reaction. In the same manner, digallane **2** reacts with 3,6-di-*tert*-butyl-*ortho*-benzoquinone (3,6-Q),[62] acenaphthenequinone, SO_2, and Ph−N═N−Ph.[63] It is worth noting that oxide **3** is a rare example of stabilization of a Ga(μ^2-O)$_2$Ga core with a chelating ligand or bulky aryl substituent. Only three compounds of this types are reported: (dpp-nacnac)Ga(μ^2-O)$_2$Ga(dpp-nacnac),[66,67] [(dpp-DAB)Ga(μ^2-O)]$_2$[K(tmeda)]$_2$ (dpp-DAB = {N(dpp)C(H)}$_2$),[68] and Ar′Ga(μ^2-O)$_2$GaAr′ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)$_2$).[69] These compounds have been prepared by reacting N_2O with gallenes [(dpp-nacnac)Ga:],[70] [(dpp-DAB)Ga:][K(tmeda)],[56] and digallene Ar′Ga−GaAr′,[69] correspondingly. On the other hand, oxide **3** is the first paramagnetic μ^2 oxo-bridged gallium derivative. Oxidation of digallane **2** by an equimolar amount of O_2 results in an intractable mixture of products besides free dpp-Bian. The reaction of O_2 with [(dpp-DAB)Ga:][K(tmeda)] proceeds similarly.[68] The stretching vibrations of the sesquialteral C−N bonds in dpp-Bian radical-anion in complex **3** results in the absorption at 1539 cm^{-1} in the IR spectrum. Despite the presence of the radical-anionic ligands, compound **3** does not exhibit a resolved isotropic ESR signal. This is indirect proof of a biradical character of compound **3**. Unfortunately, attempts to detect the corresponding signal for biradical species in a glassy toluene matrix were unsuccessful.

Desired dihydride (dpp-Bian$^{\bullet-}$)GaH_2 (**4**) has been synthesized by a treatment of oxide **3** with four molar equivalents of $PhSiH_3$ (Scheme 3). With the lesser amount of the silane, the intermediate silanolate (dpp-Bian$^{\bullet-}$)Ga{OSi(Ph)H_2}H (**5**) could be isolated (Scheme 3).

Scheme 3. Hydrogenation of the Oxide 3 by $PhSiH_3$. Formation of the Compounds 4 and 5



The formation of compounds **4** and **5** suggests that another product of the reaction is siloxane $H_2(Ph)SiOSi(Ph)H_2$, which however was not isolated. It is worth noting that dihydride (dpp-nacnac)GaH_2 can be prepared either by the exchange reaction of the (dpp-nacnac)GaI_2 with LiH·BEt_3,[31] or by the oxidative addition of dihydrogene to [(dpp-nacnac)Ga:].[32,70] Recently we have demonstrated that digallane **2** reacts with transition metal carbonyls to afford transition-metal complexes with carbenoide [(dpp-Bian$^{\bullet-}$)Ga:].[61] However, this gallium carbenoide was not detected in solution of digallane **2** in toluene or thf even under UV irradiation or at elevated temperatures. Hence, digallane **2** is unreactive toward H_2. In contrast, gallenes containing bulky aryl groups GaAr″ (Ar″ = C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)$_2$, C_6H_3-2,6-(C_6H_2-2,6-Pr^i_2-4-Bu^t)$_2$, C_6H_3-2,6-(C_6H_2-2,4,6-Pr^i_3)$_2$) are monomers in solution even at room temperature.[71,72] Compound Ga[C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)$_2$] reacts with H_2 (25 °C, 1 atm) to give the μ^2-bridged dimeric hydride complex.[73] The hydrides **4** and **5** have been isolated as brown crystals from diethyl ether in 47 and 53% yield, correspondingly. The IR spectra of compounds **4** and **5** consist of the absorption (**4**: 1547 cm^{-1}; **5**: 1545 cm^{-1}), which is characteristic for sesquialteral C−N bonds in dpp-Bian radical-anion. The presence of the Ga−H bonds in the IR spectra of **4** and **5** is manifested by the absorption at 1897 and 1872 cm^{-1} for **4** and 1939 and 1876 cm^{-1} for **5**. The stretching vibrations of Si−H bond in complex **5** results in the band at 2119 cm^{-1}. Monomeric derivative **4** reveals well-resolved ESR signal at 298 K (Figure 2).

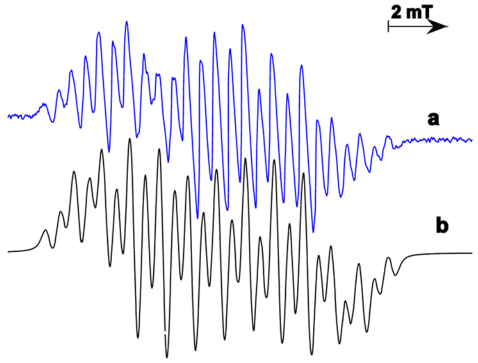


Figure 2. ESR spectrum of compound **4** (Et_2O, 298 K): (a) experimental; (b) simulated ($a_i(2 \times {}^{14}N) = 0.50$, $a_i(2 \times {}^{1}H) = 1.06$, $a_i({}^{69}Ga) = 2.03$, $a_i({}^{71}Ga) = 2.58$ mT; g = 2.0023).

The ESR spectrum of complex **5** at 293 K is also well-resolved. However, even at first glance, the presence of at least two paramagnetic compounds in solution is evident (Figure 3a). A careful simulation of the major signal and of the signal of paramagnetic impurity allowed us to conclude that the former one belongs to complex **5** (Figure 3b), while the latter signal corresponds to an admixture (5−7%) of complex **4** (Figure 3c).

The dihydride **4** can be synthesized by also reacting $PhSiH_3$ with the gallium pinacolate and catecholate, (dpp-Bian$^{\bullet-}$)Ga($O_2C_2H_2Ph_2$) (**6**) and (dpp-Bian$^{\bullet-}$)Ga(Cat) (Cat = [3,6-Q]$^{2-}$) (**7**), which can be prepared reacting **2** with Ph(H)CO and 3,6-di-*tert*-butyl-*ortho*-benzoquinone (3,6-Q)[62] correspondingly. Complex **7** has been synthesized recently[62] and used in situ. Pinacolate **6** was isolated as brown crystals from diethyl ether in 53% yield (Scheme 4).

As for the compounds **1**, **3**, **4**, and **5**, the IR spectroscopy confirms the presence of dpp-Bian radical-anion in complex **6** (ν(C−N) 1543 cm^{-1}). The ESR spectrum of pinacolate **6** in toluene at 298 K shows the coupling of an unpaired electron to two pairs of the protons (naphthalene part), to two equivalent nitrogen atoms, and to gallium isotopes ^{69}Ga and ^{71}Ga (Figure 4).

To date, only two structurally characterized gallium pinacolates have been reported: Me_5Ga_3[OC(C_6H_5)$_2$C(C_6H_5)$_2$O]$_2$[74] and tBu_3Ga_2[OC(CH_3)$_3$C(CH_3)$_2$O][OC(CH_3)$_3$C(CH_3)$_2$OH].[75] Thus, complex **6** represents the first mononuclear gallium pinacolate.

As complex **1**, compound **4** is unreactive toward heptene-1 and phenylacetylene. On the other hand, we have found that 5 mol % of compound **4** catalyzes the addition of $PhSiH_3$ to Ph(H)CO (1 to 3 molar ratio) in benzene at ambient

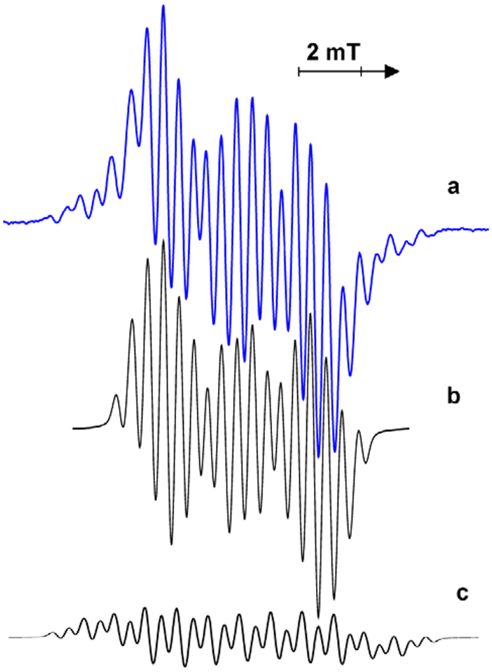
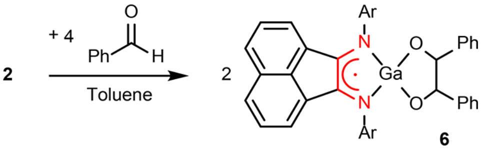


Figure 3. ESR spectrum of compound **5** (Et_2O, 298 K): (a) experimental; (b) simulated for BIANGa(H)OSi(H)$_2$Ph ($a_i(2 \times {}^{14}N) = 0.46$, $a_i(1 \times {}^{1}H) = 0.60$, $a_i({}^{69}Ga) = 1.38$, $a_i({}^{71}Ga) = 1.75$ mT; $g = 2.0020$); (c) simulated for **4**.

Scheme 4. Formation of the Pinacolate 6 from Digallane 2



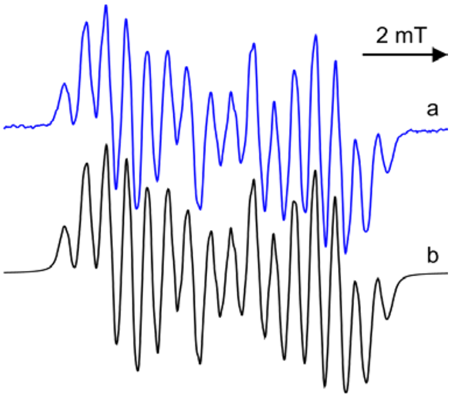
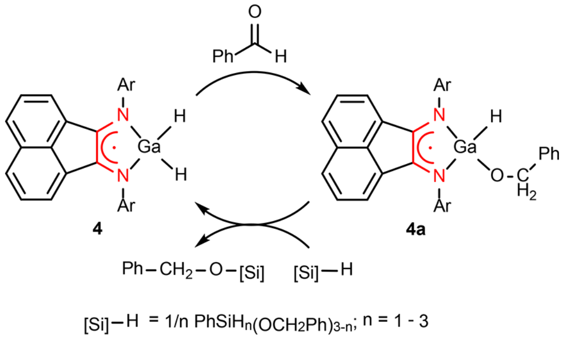


Figure 4. EPR spectrum of compound **6** (toluene, 298 K): (a) experimental; (b) simulated ($a_i(2 \times {}^{1}H) = 0.090$, $a_i(2 \times {}^{1}H) = 0.128$, $a_i(2 \times {}^{14}N) = 0.442$, $a_i({}^{69}Ga) = 1.445$, $a_i({}^{71}Ga) = 1.836$ mT; $g = 2.0025$).

temperature. Within 7 h, the conversion of the starting materials into $PhSi(OCH_2Ph)_3$ reaches 99% (NMR). A tentative catalytic cycle for hydrosilylation of benzaldehyde by phenylsilane in the presence of compound **4** is depicted in Scheme 5. It should be also mentioned that some strong bases (e.g., *t*BuOK[76]) catalyze efficient addition of [Si–H] substrates to carbonyl compounds.

Scheme 5. Tentative Catalytic Cycle for Hydrosilylation of Benzaldehyde by Phenylsilane in the Presence of Compound 4



In order to synthesize gallium hydride species coordinated to dpp-Bian *dianion*, we have reacted compound **1** with sodium metal (one molar equivalent) in diethyl ether. Unfortunately, this reaction resulted in an intractable mixture of product. The reaction of complex (dpp-Bian$^{\bullet-}$)$GaCl_2$ with $LiAlH_4$ in THF affords the aluminum complex of dpp-Bian dianion, [(dpp-Bian^{2-})Al(μ-Cl)$_2$Li(thf)$_3$], as a single isolable product. Its synthesis and characterization will be published elsewhere. Just recently, we have prepared the aluminum counterpart of the desired gallium hydride. Thus, the reaction of (dpp-Bian^{2-})Na_2 with Cl_2AlH in diethyl ether affords aluminum hydride with dpp-Bian dianion, (dpp-Bian^{2-})AlH(Et_2O).[77] Unexpectedly, an analogous reaction between (dpp-Bian^{2-})Na_2 and Cl_2GaH in Et_2O afforded NaCl, digallane (dpp-Bian^{2-})Ga–Ga(dpp-Bian^{2-}), and unidentified products.

Molecular Structures of 1, 3, 4, 5, and 6. Molecular structures of compounds **1**, **3**, **4**, **5**, and **6** (Figures 5, 6, 7, 8 and 9, correspondingly) have been determined by single crystal X-ray analysis. The crystal data and structure refinement details are listed in Table S1.

In all the molecules, the gallium atoms reveal a slightly distorted tetrahedral environment. The reduction state of the dpp-Bian ligand (0, −1, or −2) in its metal complexes can be easily deduced from the analysis of the bond lengths within the diimine moiety. Thus, moving from the neutral to radical-anionic and further to dianionic dpp-Bian the C(1)–N(1) and

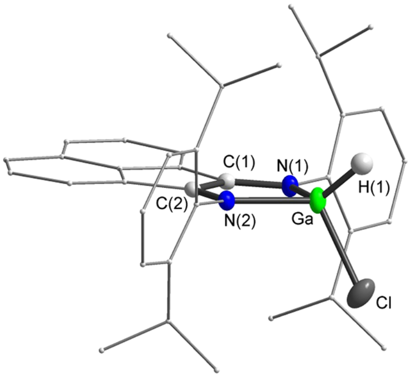


Figure 5. Molecular structure of **1**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms with the exception of H(1) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga–Cl 2.1535(8), Ga–N(1) 1.958(2), Ga–N(2) 1.952(2), N(1)–C(1) 1.327(3), N(2)–C(2) 1.326(3), C(1)–C(2) 1.425(3); N(1)–Ga–N(2) 86.06(7).

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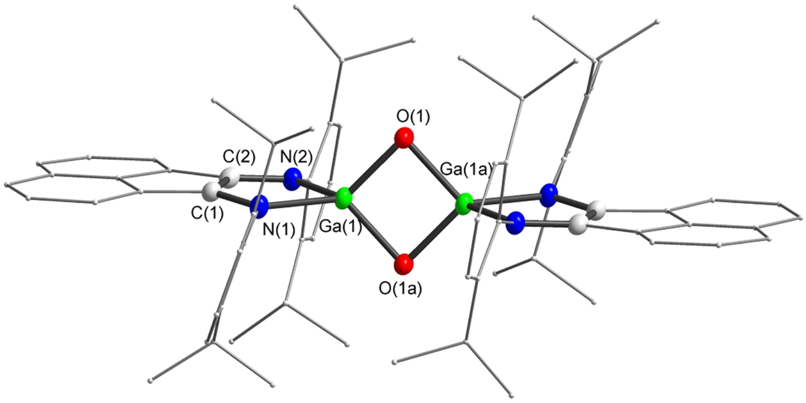

Figure 6. Molecular structure of **3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)−O(1) 1.842(2), Ga(1)−O(1A) 1.837(2), Ga(1)---Ga(1A) 2.5464(6), Ga(1)−N(1) 1.979(2), Ga(1)−N(2) 1.959(2), N(1)−C(1) 1.343(3), N(2)−C(2) 1.336(3), C(1)−C(2) 1.436(4); O(1)−Ga(1)−O(1a) 92.38(8), Ga(1)−O(1)−Ga(1A) 87.62(8), N(1)−Ga(1)−N(2) 86.54(9).

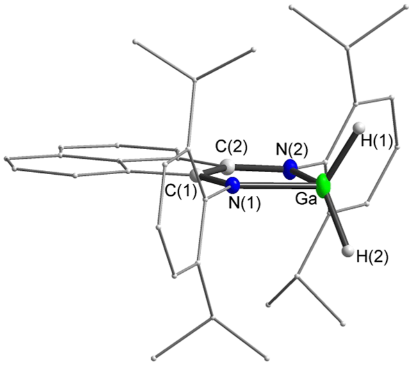

Figure 7. Molecular structure of **4**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms with the exception of H(1) and H(2) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga−H(1) 1.53(2), Ga−H(2) 1.47(2), Ga−N(1) 1.983(2), Ga−N(2) 1.997(2), N(1)−C(1) 1.324(2), N(2)−C(2) 1.329(2), C(1)−C(2) 1.435(2); H(1)−Ga−H(2) 122.5(13), N(1)−Ga−N(2) 84.76(5).

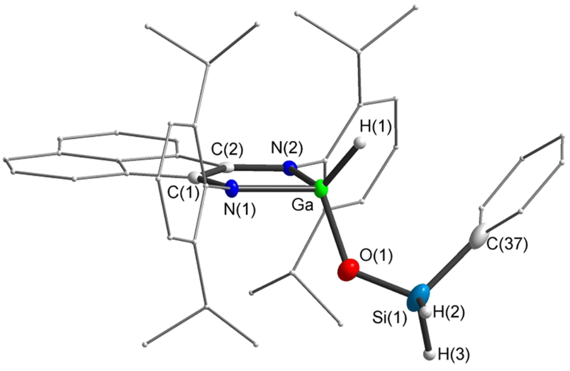

Figure 8. Molecular structure of **5**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms with the exception of H(1), H(2), and H(3) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga−H(1) 1.49(3), Ga−O(1) 1.807(2), Ga−N(1) 1.951(2), Ga−N(2) 1.973(2), N(1)−C(1) 1.331(3), N(2)−C(2) 1.332(3), C(1)−C(2) 1.436(3), Si(1)−O(1) 1.609(2); H(1)−Ga−O(1) 116.5(13), N(1)−Ga−N(2) 85.89(8), Ga−O(1)−Si(1) 129.3(2), O(1)−Si(1)−C(37) 109.8(2).

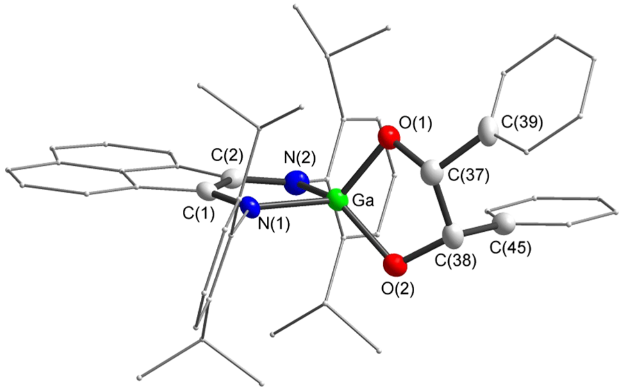

Figure 9. Molecular structure of **6**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga−O(1) 1.830(3), Ga−O(2) 1.826(3), Ga−N(1) 1.946(3), Ga−N(2) 1.949(3), N(1)−C(1) 1.337(5), N(2)−C(2) 1.336(5), C(1)−C(2) 1.445(5), C(37)−O(1) 1.423(5), C(38)−O(2) 1.439(5), C(37)−C(38) 1.571(6), C(37)−C(39) 1.511(5), C(38)−C(45) 1.507(6); O(1)−Ga−O(2) 94.2(2), N(1)−Ga−N(2) 86.5(2), Ga−O(1)−C(37) 104.2(2), Ga−O(2)−C(38) 106.9(2), O(1)−C(37)−C(38) 108.1(3), O(2)−C(38)−C(37) 107.5(3), O(1)−C(37)−C(39) 111.7(3), O(2)−C(38)−C(45) 112.8(3).

C(2)−N(2) bonds become longer, while the C(1)−C(2) bond becomes shorter. These geometrical changes reflect a population of the LUMO of dpp-Bian in the course of its reduction. In complexes **1**, **3**, **4**, **5**, and **6**, the corresponding values lie in a narrow range (C(1)−N(1), 1.324(2)−1.343(3) Å; C(2)−N(2), 1.326(3)−1.336(3) Å; and C(1)−C(2), 1.425(3)−1.445(5) Å) and confirm unambiguously the radical-anionic states of the dpp-Bian ligands. These bonds compare to those in paramagnetic complexes (dpp-Bian$^{\bullet-}$)-GaX$_2$ (X = Cl,[54] I,[51] SCH$_2$Ph,[53] CCPh[55] and N(H)Ph;[78] both C−N, 1.33 Å (average) and C(1)−C(2), 1.43 Å (average)). Also, the bonds Ga−N(1) (1.951(2)−1.983(2) Å) and Ga−N(2) (1.952(2)−1.997(2) Å) are close to those values in gallium complexes of dpp-Bian radical-anion.[51,53−55,61−63,78]

The oxide **3** is a centrosymmetric dimer. The gallium atoms are connected via two O^{2-} ligands. The almost square core Ga(μ^2-O)$_2$Ga forms the plane, which is practically orthogonal (89.4°) to the planes estimated with the C and N atoms of the diimine moieties. The difference in Ga(1)−O(1) (1.842(2) Å) and Ga(1)−O(1a) (1.837(2) Å) bond lengths is as small as 0.005 Å. These bond lengths are close to those in the ketiminate derivative [(dpp-nacnac)Ga(μ^2-O)]$_2$ (1.8536(9) and 1.8485(9) Å).[66] On the other hand, two Ga−O bonds in diazadiene derivative [(dpp-DAB)Ga(μ-O)]$_2$[K(tmeda)]$_2$ differ significantly (1.814(3) and 1.905(3) Å).[68] In complex **3**, the Ga---Ga separation (2.5464(6) Å) is 0.03 Å longer than the Ga−Ga bond in digallane (dpp-Bian$^{\bullet-}$)Ga(μ^2-AcQ)Ga(dpp-Bian$^{\bullet-}$) (2.5159(6) Å),[63] and 0.03 Å shorter than the Ga−Ga bond in digallane (dpp-DAB)IGa−GaI(dpp-DAB) (2.576(2) Å).[47]

The parameters of the fragments H−Ga−X in **1** (X = Cl), **4** (X = H), and **5** (X = OSiPhH$_2$) can be compared to each other as well as with those parameters of the related gallium hydrides. For complex **1**, this comparison is not entirely correct because the Ga−H distance in **1** was fixed in the course of the structure refinement. Nevertheless, the Ga−Cl bond length in complex **1** has been determined rather accurately (2.1535(8) Å). It is practically identical with those values in dichlorgallane H(Cl)Ga(μ^2-Cl)$_2$Ga(Cl)H (2.1538(5) Å)[11] and in complex (dpp-Bian$^{\bullet-}$)GaCl$_2$ (average 2.153 Å).[54] On the other hand, the Ga−Cl bond in complex **1** is shorter compared to the corresponding bonds in {[Me$_2$NCH$_2$CMe$_2$CH$_2$(H)N]Ga(Cl)-H}$_2$ (2.2478(8) Å)[79] and [(hpp)Ga(Cl)H]$_2$ (2.202(2) Å) (hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidate).[80]

The Ga−H bond lengths in complex **4** (1.53(2) and 1.47(2) Å) fall in to the range of those lengths in gallium dihydrides [(*t*Bu-DAB)GaH]$_2$ (1.46(6) Å),[29] [(dpp-DAB)GaH$_2$][Li-(thf)$_2$] (1.55(4) and 1.54(5) Å)[30] and (dpp-nacnac)GaH$_2$ (1.52(2) and 1.54(2) Å).[31] The Ga−H bond in silanolate **5** (1.49(3) Å) is comparable to those bonds in the related (dpp-nacnac)GaH(OSi(Ph)$_2$OH) (1.42(2) Å),[35] [(OSiPh$_2$OSiPh$_2$O)[Ga(H)]$_2$(O*t*Bu)$_2$] (average 1.44(5) Å) and [(OSiPh$_2$OSiPh$_2$OSiPh$_2$O)GaH]$_2$ (1.38(6) Å).[81] The Ga−O(Si) bond in complex **5** (1.807(2) Å) is close to those in (dpp-nacnac)GaH(OSi(Ph)$_2$OH) (1.830(1) Å), [(OSiPh$_2$OSiPh$_2$OSiPh$_2$O)GaH]$_2$ (1.919(2) Å) and [(OSiPh$_2$OSiPh$_2$O)[Ga(H)]$_2$(O*t*Bu)$_2$] (average 1.789(3) Å). The angle H(1)−Ga−O(1) in silanolate **5** (116.5(13)°) is well compared with that in (dpp-nacnac)GaH(OSi(Ph)$_2$OH) (114.2(8)°).

The carbon atoms C(37) and C(38) in the pinacolate ligand in complex **6** (Figure 9) are chiral. The unit cell (Z = 4) consist of two enantiomeric pairs, (*R*)-C(37)−(*S*)-C(38) and (*S*)-C(37)−(*R*)-C(38). The metalacycle −Ga−O(1)−C(37)−C(38)−O(2)− exhibits a conformation of a “half-chair”. The torsion angle C(39)−C(37)−C(38)−C(45) is 47.1°. The distance between the centroids of the phenyl rings in the pinacolate ligand (4.39 Å) is 0.34 Å shorter than that distance in D-(+)-hydrobenzoin (4.73 Å).[82] The bond C(37)−C(38) (1.571(6) Å) is elongated compared to corresponding bond in D-(+)-hydrobenzoin, while the bonds C(37)−O(1) (1.423(5) Å) and C(38)−O(2) (1.439(5) Å) are close to those in D-(+)-hydrobenzoin (1.538(4), 1.424(4) and 1.435(4) Å). The Ga−O bond lengths (1.830(3) and 1.826(3) Å) in compound **6** are shorter than those bond lengths in the related pinacolates *t*Bu$_3$Ga$_2$[OC(CH$_3$)$_3$C(CH$_3$)$_2$O][OC(CH$_3$)$_3$C(CH$_3$)$_2$OH] and Me$_5$Ga$_3$[OC(C$_6$H$_5$)$_2$C(C$_6$H$_5$)$_2$O]$_2$ (1.859(3)−2.180(3) Å), while the angle O(1)−Ga−O(2) (94.2(2)°) is larger compared to the pinacolates mentioned above (75.6(1)−84.7(1)°).[74,75] This difference in the bond lengths and angles reflects the difference in the coordination number of complex **6** (CN = 4) and in the alkylgalliumpinacolates (CN = 5).

■ CONCLUSION

In this paper, we reported the synthesis and characterization of the first gallium hydride derivatives that consist of the paramagnetic radical-anionic ligand, namely, acenaphthene-1,2-diimine, (dpp-Bian$^{\bullet-}$)Ga(X)H (**X** = Cl, **1**; H, **4**; OSi(Ph)-H$_2$, **5**). Due to the bulkiness and rigidity of the dpp-Bian ligand, the complexes **1**, **4**, and **5** represent monomeric four-coordinate gallium species. Two synthetic approaches have been used for the preparation of desired compounds: (i) the salt elimination exchange reaction; (ii) hydrogenation of the Ga−O bond with PhSiH$_3$. The latter approach seems to be more useful because it allows the preparation of gallium mono- as well as dihydrides. The presence of the dpp-Bian radical anion in the complexes **1**, **4**, and **5** both in solution and in the solid state has been unambiguously confirmed by the ESR spectroscopy and X-ray crystallography.

Recently, we have shown that in alkylaluminum complexes, the dpp-Bian is acting rather as stabilizing ligand toward alkyl−aluminum bond. For instance, Ph$_2$C=O and PhC≡CH do not insert into the Al−C(Et) bond in compound (dpp-Bian^{2-})-AlEt(Et$_2$O): the ketone replaces the coordinating solvent, while the alkyne forms the cycloadduct through the formation of C−C and C−Al bonds.[83] The situation seems to be similar to gallium hydrides **1** and **4**. They do not react with the unsaturated substrates (e.g., alkenes and alkynes). However, dihydride **4** catalyzes addition of PhSiH$_3$ to Ph(H)C=O. This reaction proceeds presumably through the insertion of the latter into the Ga−H bond. On the other hand, instability of the Ga−H bond in the presence of the dpp-Bian dianion reveals the difference between aluminum and gallium species. Thus, compound (dpp-Bian^{2-})AlH(Et$_2$O) can be prepared straightforwardly by reacting (dpp-Bian^{2-})Na$_2$ with Cl$_2$AlH, while the reaction of (dpp-Bian^{2-})Na$_2$ with Cl$_2$GaH in Et$_2$O gives digallane (dpp-Bian^{2-})Ga−Ga(dpp-Bian^{2-}).

■ EXPERIMENTAL SECTION

General Remarks. The newly obtained compounds **1** and **3**−**6** are sensitive to oxygen and air moisture, so all manipulations for their synthesis, isolation, and identification were carried in a vacuum using glass ampules. The dpp-Bian was prepared by the condensation of acenaphthenequinone with 2,6-diisopropylaniline (both from Aldrich) in acetonitrile under reflux. The 3,6-di-*tret*-bytyl-*orto*-benzoquinone[84] and dichlorogallane[11] were synthesized according to known techniques. Nitrous oxide (N$_2$O) was synthesized by reaction of sulfamic acid (H$_2$NSO$_3$H) with HNO$_3$ (73%), then passed through solid NaOH and P$_4$O$_{10}$ powder for purification and drying. The compound (dpp-Bian$^{\bullet-}$)Na was obtained by the reaction of dpp-Bian (2 g, 4.0 mmol) with sodium (0.092 g, 4.0 mmol) in diethyl ether (50 mL) and used in situ in the reaction with dichlorogallane. Digallane (dpp-Bian^{2-})Ga−Ga(dpp-Bian^{2-}) (**2**) was prepared by reflux of dpp-Bian (0.5 g, 1.0 mmol) with an excess of gallium metal in toluene (30 mL) and used in situ in the reactions described below. The yields of the products were calculated from the starting amount of the dpp-Bian. Phenylsilane (CAS 694-53-1) and benzaldehyde (CAS 100-52-7) were purchased from Aldrich and dried over CaH$_2$ prior to use. Toluene and diethyl ether were dried by distillation from sodium benzophenone. The melting points were determined in sealed capillaries. The IR spectra were recorded on a FSM-1201 instrument in mineral oil. The ESR spectra were recorded on a Bruker EMX spectrometer (9.75 GHz); the signals were referred to the signal of diphenylpicrylhydrazyl (g = 2.0037) and simulated with the WinEPR SimFonia Software (Bruker).

(dpp-Bian$^{\bullet-}$)Ga(Cl)H (1). To a solution of (dpp-Bian$^{\bullet-}$)Na (in situ from 2.0 g, 4.0 mmol of dpp-Bian) in diethyl ether (50 mL), the dichloroglanane (0.56 g, 4.0 mmol) was added. The mixture was stirred for 30 min, and the resulting NaCl was filtered off. After replacing the diethyl ether with toluene, the resulting brown solution was concentrated (20 mL) under vacuum. In the course of 24 h at 10 °C, brown crystals of (dpp-Bian)Ga(Cl)H precipitated (1.77 g, 73%). mp = 285 °C. Anal. Calcd for $C_{36}H_{41}ClGaN_2$ (606.88): C, 71.25; H, 6.81; N, 4.62; Cl, 5.84. Found: C, 71.49; H, 6.89; N, 4.66; Cl, 5.65%. IR (mineral oil): 1951 (s) (Ga−H), 1893 (w) (Ga−H), 1866 (m) (Ga−H), 1820 (w), 1805 (w), 1732 (w), 1672 (w), 1598 (m), 1583 (w), 1545 (s), 1426 (m), 1363 (m), 1324 (s), 1253 (m), 1214 (m), 1189 (m), 1149 (m), 1114 (m), 1080 (w), 1054 (m), 1037 (w), 1007 (w), 968 (w), 951 (s), 933 (m), 897 (w), 876 (w), 819 (m), 802 (m), 774 (m), 762 (s), 748 (w), 672 (m), 656 (m), 641 (w), 590 (w), 558 (w), 547 (w) 516 (w), 504 (w). ESR (toluene, 298 K): $a_i(2 \times {}^{14}N) = 0.476$, $a_i(1 \times {}^{1}H) = 0.590$, $a_i({}^{35}Cl) = 0.219$, $a_i({}^{37}Cl) = 0.183$, $a_i({}^{69}Ga) = 1.423$, $a_i({}^{71}Ga) = 1.807$ mT; g = 2.0021.

(dpp-Bian$^{\bullet-}$)Ga(μ^2-O)$_2$Ga(dpp-Bian$^{\bullet-}$) (3). To a solution of **2** (in situ from 0.5 g, 1.0 mmol of dpp-Bian) in toluene (30 mL), N_2O (24 mL, 1.0 mmol) was added at −95 °C, and the ampule was sealed under vacuum. An increase in the temperature of the reaction mixture to 20 °C was accompanied by evolution of N_2 and a color change from deep blue to red-brown. After 4 days, the dark-green crystals of oxide **3** (0.42 g, 72%) were isolated. mp > 250 °C. Anal. Calcd for $C_{72}H_{80}GaN_4O_2$ (1172.84): C, 73.74; H, 6.88; N, 4.78. Found: C, 73.89; H, 6.82; N, 4.63%. IR (mineral oil): 1592 (w), 1539 (s), 1379 (w), 1363 (m), 1321 (m), 1255 (m), 1211 (w), 1185 (w), 1144 (w), 1112 (w), 1060 (w), 1040 (w), 821 (m), 801 (s), 774 (s), 764 (s), 760 (s), 606 (s), 596 (s), 547 (m).

(dpp-Bian$^{\bullet-}$)GaH$_2$ (4). Method A. To a suspension of compound **3** (0.36 g, 0.3 mmol) in diethyl ether (20 mL), $PhSiH_3$ (0.13 g, 1.2 mmol) was added. Oxide **3** dissolved completely, and the color of reaction mixture turned to brown. Brown crystals of dihydride **4** (0.16 g, 47%) were separated from concentrated Et_2O solution. **Method B.** To a solution of compound **2** (in situ from 0.5 g, 1.0 mmol of dpp-Bian) in toluene (30 mL), phenylsilane (0.216 g, 2.0 mmol) and benzaldehyde (0.212 g, 2.0 mmol) were consequently added. The color of the reaction mixture changed to brown. Toluene was removed in vacuum, and the residue was dissolved in diethyl ether (10 mL). Crystallization from diethyl ether gave the compound **4** (0.18 g, 31%). **Method C.** To a solution of compound **2** (in situ from 0.5 g, 1.0 mmol of dpp-Bian) in toluene (30 mL), 3,6-di-*tret*-bytyl-*orto*-benzoquinone (0.22 g, 1.0 mmol) was added. The ampule was sealed off and heated at 80 °C. Within 2 h, the reaction mixture turned green. Then ampule was opened and $PhSiH_3$ (0.216 g, 2.0 mmol) was added to the reaction mixture. The ampule was sealed off again and heated at 80 °C until the color of reaction mixture changed from green to brown. Then solvent was removed in vacuum, and the residue was dissolved in diethyl ether. Crystallization from diethyl ether afforded compound **4** (0.25 g, 44%). mp > 250 °C. Anal. Calcd for $C_{36}H_{42}GaN_2$ (572.43): C, 75.54; H, 7.40; N, 4.88. Found: C, 75.96; H, 7.48; N, 4.72%. IR (mineral oil): 1897 (s) (Ga−H), 1872 (s) (Ga−H), 1615 (m), 1597 (m), 1547 (s), 1323 (s), 1256 (m), 1211 (s), 1188 (m), 1115 (m), 1053 (m), 1040 (m), 933 (m), 823 (s), 814 (s), 802 (s), 781 (s), 764 (s), 744 (s), 696 (s), 675 (s), 663 (m), 615 (w), 596 (w), 551 (w), 505 (s). ESR (toluene, 298 K): $a_i(2 \times {}^{14}N) = 0.50$, $a_i(2 \times {}^{1}H) = 1.00$, $a_i({}^{69}Ga) = 1.92$, $a_i({}^{71}Ga) = 2.44$ mT; g = 2.0025.

(dpp-Bian$^{\bullet-}$)Ga{OSi(Ph)H$_2$}H (5). To a suspension of compound **3** (0.36 g, 0.3 mmol) in diethyl ether (30 mL), $PhSiH_3$ (0.065 g, 0.6 mmol) was added. Oxide **3** dissolved, and the color of reaction mixture turned to brown. Brown crystals of complex **5** (0.22 g, 53%) were separated from concentrated Et_2O solution. Calcd for $C_{42}H_{48}GaN_2OSi$ (694.63): C, 72.62; H, 6.97; N, 4.03. Found: C, 71.82; H, 7.03; N, 3.94%. mp = 190 °C. IR (mineral oil): 2119 (s) (Si−H), 1939 (s) (Ga−H), 1876 (w) (Ga−H), 1594 (s), 1545 (s), 1430 (s), 1362 (m), 1327 (s), 1264 (m), 1213 (m), 1188 (m), 1117 (s), 970 (s), 897 (s), 825 (m), 814 (s), 808 (m), 764 (s), 764 (s), 739 (s), 702 (s), 652 (m), 644 (m), 630 (s), 615 (w), 557 (w), 499 (s).

(dpp-Bian$^{\bullet-}$)Ga(O$_2$C$_2$H$_2$Ph$_2$) (6). To a solution of compound **2** (in situ from 0.5 g, 1.0 mmol of dpp-Bian) in toluene (30 mL), benzaldehyde (0.212 g, 2.0 mmol) was added. The color of the reaction mixture changed to red. The solvent was removed in vacuum, and the residue was dissolved in diethyl ether (10 mL). The compound **6** was isolated (0.45 g, 53%) by crystallization from the concentrated solution. Calcd for $C_{53.34}H_{60.35}GaN_2O_{2.84}$ (844.54): C, 75.86; H, 7.20; N, 3.32. Found: C, 76.81; H, 7.14; N, 3.52%. Mp = 86 °C. IR (mineral oil): 1598 (m), 1585 (w), 1543 (s), 1365 (s), 1350 (s), 1307 (m), 1265 (m), 1254 (m), 1215 (m), 1203 (w), 1185 (m), 1149 (m), 1118 (s), 1077 (m), 1058 (w), 1034 (s), 1023 (s), 971 (w), 951 (w), 936 (w), 894 (w), 882 (w), 869 (w), 844 (w), 821 (s), 802 (s), 771 (s), 761 (s), 746 (s), 712 (s), 697 (s), 675 (s), 670 (m), 650 (m), 637 (m), 610 (s), 562 (m), 545 (w), 517 (w), 507 (w). ESR (toluene, 298 K): $a_i(2 \times {}^{1}H) = 0.090$, $a_i(2 \times {}^{1}H) = 0.128$, $a_i(2 \times {}^{14}N) = 0.442$, $a_i({}^{69}Ga) = 1.445$, $a_i({}^{71}Ga) = 1.836$ mT; g = 2.0025.

X-ray Crystallography. The X-ray data for **1** and **3**−**6** were collected on Bruker Smart Apex (**3**), Bruker D8 Quest (**1**, **5**), and Agilent Xcalibur E (**4**, **6**) diffractometers (Mo Kα radiation, ω-scans technique, $\lambda = 0.71073$ Å, $T = 100(2)$ K) using SMART, APEX2,[85] and CrysAlis PRO[86] software packages. The structures were solved by direct and dual-space[87] methods and were refined by full-matrix least-squares on F^2 for all data using SHELX.[88] SADABS[89] and CrysAlis PRO were used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. Hydrogen atoms of hydride ligands in **1**, **3** and **5** also were found from Fourier syntheses of electron density and were refined isotropically. Other hydrogen atoms in **1** and **3**−**6** were placed in calculated positions and were refined in the "riding" model with $U(H)_{iso} = 1.2U_{eq}$ of their parent atoms ($U(H)_{iso} = 1.5U_{eq}$ for methyl groups).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02138.

Crystallographic data and structure refinement details for **1**, **3**−**6** are given in Table S1 (PDF)

Accession Codes

CCDC 1569549−1569553 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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